

Nanoprobe maskless lithography

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ABSTRACT

Scanning probe-based methods for surface modification and lithography are an emerging method of producing sub 20-nm features for nanoelectronic applications. In this study, we have demonstrated the nanoscale lithography based on patterning of 10 to 50-nm-thick calix[4]arene by electric-field-induced electrostatic scanning probe lithography. The features size control is obtained using electrostatic interactions and depends on the applied bias and speed of the AFM tip. The width of the obtained lines and dots varies from 10 to 60 nm depending on tip-sharpness, tip-substrate separation and tip-bias voltage.

Keywords: scanning probe lithography (SPL), atomic force microscopy, nanofabrication, self-assembled calixarene monolayers.

1. INTRODUCTION

High performance Single Nanometer Lithography (SNL) is an enabling technology for nanoelectronics. The principles of physics allows building of transistors or memory cells with dimensions in the order of single nanometer, (e.g. single electron or spin based devices); however, new SNL techniques must be developed to realize these devices. This has led to an interest in the new nanolithographic methods based on proximal scanning probes. Scanning Probe Microscopes (SPM) were originally developed to observe physical or biological surfaces at the nanoscale, but almost immediately after their invention, high resolution scanning-probe lithography (SPL) was demonstrated [1]. SPM techniques for surface modification and lithography include atomic manipulation and positioning [2], thermomechanical modification [3], dip-pen nanolithography [4], nanografting [5], STM local-probe oxidation [6]. In addition, AFM - electrostatic nanolithography (AFMEN) [7] has also been demonstrated and investigated intensively in the group of Lyuksyutov [8-10]. In this technique, nanolithography is achieved by modifying polymer films with electrostatic fields created between the tip and sample. Because this is in non-contact mode, scanning can be done at high speeds.

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SPL, in general, is extremely promising for sub-20 nm lithography with a multitude of benefits which include relatively low equipment costs, high flexibility, overlay accuracy with close to atomic resolution, direct inspection capability, and operation ease. However, the single probe tips used in SPM are a barrier to high throughput fabrication. The main objective of our work is to realize high throughput SPM and SPL techniques. Here we describe our efforts in self-actuated piezoresistive cantilevers and cantilever arrays and SPL work based on electrostatic manipulation of calixarenes for high speed single nanometer lithography.

2. SELF-ACTUATED PIEZORESISTIVE CANTILEVER AND CANTILEVER ARRAYS

Two-dimensional AFM cantilever array, such as a millipede system [11] has been employed successfully for data storage. Recently, Rangelow and co-workers reported a parallel cantilever SPM array of 2D-512 (4x64) based on a self-actuated piezoresistive cantilever set-up [12-14] (Figure 1). The goal of this work was not only to carry out a feasibility study of self-actuated piezoresistive cantilever design, but also to examine an experimental cantilever set-up relevant to imaging and SPL applications (Figure 2). The integration of the piezoresistive readout and thermally driven bimetal (bimorph) actuator provides a means to realize a compact, noncontact scanning probe microscope (SPM) capable of parallel imaging or SPL over large areas at speeds compatible with high volume production. Piezoresistive beam bending detection has advantages over conventional optical beam deflection techniques [15-20], especially in cantilever arrays.

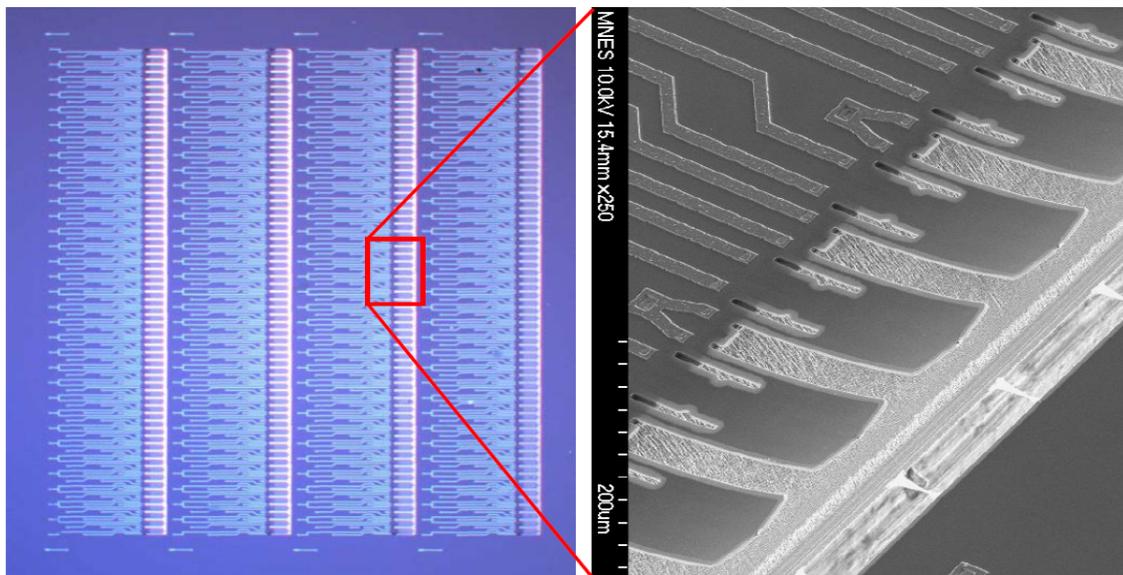


Figure 1. Optical microscope and SEM pictures of 2D-256 (64x4) self-actuated, piezoresistive cantilever array with vertical interconnections [12].

For autonomic bending control of each cantilever, signal conversion from the electrical to the mechanical domain is necessary. This can be realized by adding conversion elements compatible with complementary metal oxide semiconductor processing using thin film technology.

The microactuators described here are based on the so-called bimetal or bimorph [13-20] effect. In the previous work, we demonstrated the construction of single cantilevers with piezoresistive readout and integrated bimorph (bimetal) actuators for noncontact AFM as an alternative to optically detected devices with a piezotube z actuator (Figure 2). The feedback speed can be improved through integration of the actuator with the cantilever, providing feedback by applying an acting force to the cantilever. This significantly increases the resonance frequency compared to typical piezoelectric actuator stages in commercial systems. However, the thermal actuation has bandwidth limits which have to be overcome by optimizing the cantilever design and meet compromises in deflection amplitude. The high resonance frequency of the cantilever in combination with a larger gain, short-time-constant feedback loop determine the surface scan speed required to accurately follow surface topography. In our setup the cantilever is driven by thermal actuation at its resonance frequency f_{res} by an ac with frequency $f_{res}/2$, while the z axis actuation is provided by applying dc. The magnitude of the dc determines the deflection of the cantilever and is controlled by the proportional integral differential feedback loop.

The accurate following of surface topography for SPL is crucial. To get the highest resolution, the space between a sharp tip (can practically be even 1nm) and the surface must be as small and stable.

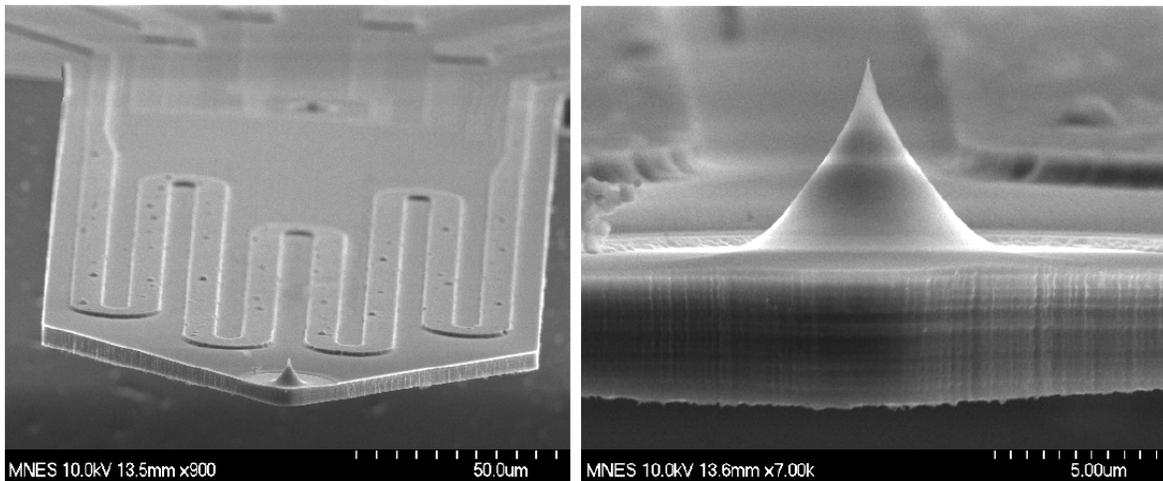


Figure 2. Self-actuated piezoresistive cantilever used for SPL.

3. SCANNING PROBE LITHOGRAPHY OF CALIXARENES

A key goal of SPM-based nanolithography is to develop and enhance sub-10-nm patterning and to assemble functional biological and chemical nanolayers. We have investigated the patterning of calixarenes for SPL because they can act as high resolution resists and functional materials for applications in sensors, catalysis, optical materials, field effect transistors and membranes [21-22]. Calixarenes [23] have been used successfully in electron beam and extreme ultra- violet lithography (EBL and EUVL) to create sub-10 nm features at dense pitches [24-25]. In EBL and EUVL applications, the calixarene acts as negative resist, whereas they are cross-linked by the incident radiation and rendered insoluble in a developer solution. Here we investigate its behaviour in scanning probe electrostatic lithography (SPEL).

Previous investigations in SPL have patterned a broad types of polymers, such as poly(methyl methacrylate) (PMMA), polystyrene (PS), polysulfone, polyaniline, and polythiophene [4-10]. The features of the nanopatterns created in the polymer films depended on the type of polymer used, the applied bias, and the speed of the AFM tip.

We expect calixarenes to be somewhat differently because they are much smaller macromolecules with special interaction within and between molecules. Calixarenes belong to a group of cyclical phenol-formaldehyde oligomers. Structurally calixarene molecules represent spatial cavities of different sizes depending on number of including phenol rings. A chalice or cone shape can be stabilized with different upper and lower rim functionalizations. In our case, we use tert-butyl calix[4]arenes with hydroxyl groups on the lower rim. The 4 hydroxyl groups on the lower rim can interact by hydrogen bonding to stabilize the cone and create an an internal volume which is approximately ten cubic nanometers. The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. Between neighboring molecules, generally van der Waals interactions are expected.

The SPL experiments on calixarene were performed in noncontact mode both with and with out applying voltage pulses to the tip. The laboratory environment secures temperature of 21°C and 60% air humidity (Figure 3).

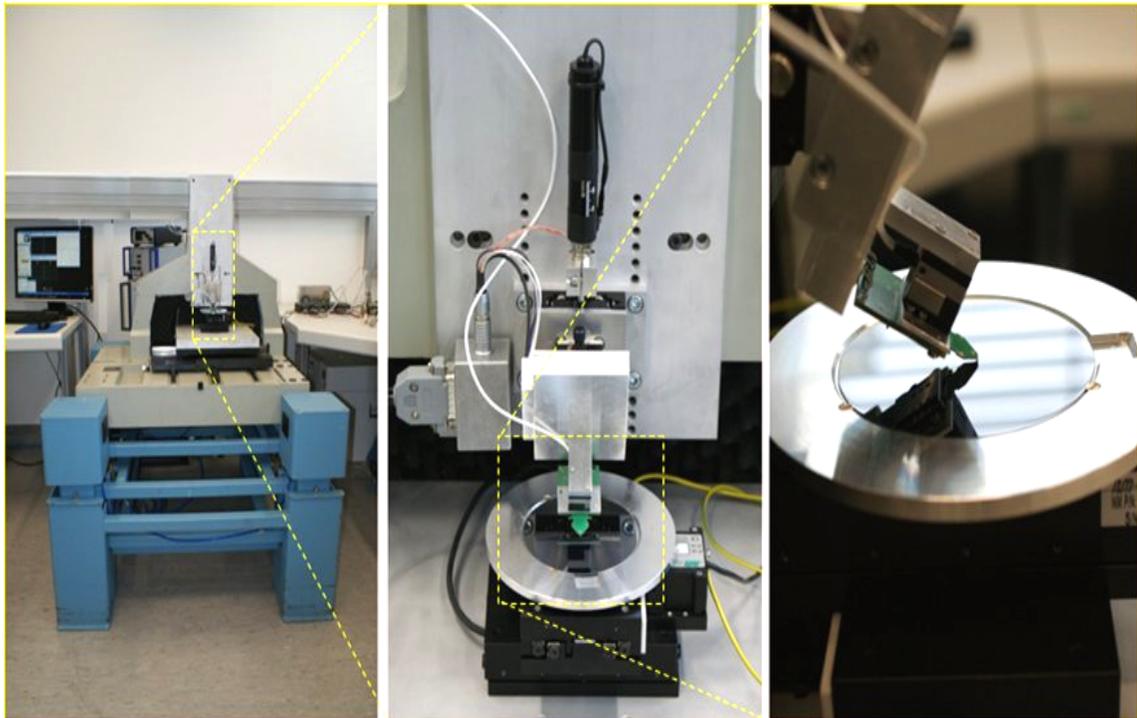


Figure 3. Nanoprobe Maskless Lithography System (NMLS). Lithography unit (left), Wafer on nanopositioning x-y stage (middle); SPL-Cantilever approaching silicon wafer (left).

The cantilever is driven at its resonance frequency of 156 kHz and the AFM tip line velocity was varied from 100 nm/s to 1000 nm/s. The present configuration consists of two independent stages, which are placed onto

each other with an angle of 90° in order to realize x- and y-axes. Each stage has a travel range of 100mm. The attached ceramic, piezoelectric motor has a maximum velocity of 250mm/s and a static holding force of around 28N. Incremental position sensors from are attached to the linear stages. These optical sensors have a resolution of 10nm and can be moved up to 65mm/s. A microcontroller with an integrated PID regulator is supplied as well as different connection possibilities to a Host computer, like Ethernet and RS232. Feedback, Feed forward, low pass filters, notch filters, etc. can be controlled by both a program running on the controller itself or by a program executed on a Host computer.

Nanostructures were generated after applying voltage pulses between the negatively biased silicon tip (deposited with 5 nm Cr/10 nm Au) and the silicon surface covered with a calixarene film. Scanning probe lithography (SPL) using polymer films as in conventional lithography is a principally simple method. In SPL, electrons injected from a tip into a polymer film can cause modifications of the polymer molecules. Current flowing between the sharp tip and the conductive substrate is tunnelling through the calixarene film. The current of 10 to 50 nA induces a highly localized Joule heating of the calixarene and excitation of its molecules. The actual extraction mechanism is not clear. Taking under account that the binding energy between the calixarene molecules is much lower than in the calixarene rings and due to the localised high electrical field (10^9 V/m), we surmise that the strongly polarised molecules can be extracted out from the film. This suggests that the features arise by mass transport of calixarene without degradation of the ring structure. With tip-biases between 25–80V, features as small as 10nm have been generated in thin calixarene films (5 to 50 nm) either deposited by evaporation or the Langmuir–Blodgett method. Using a SEM we investigate the profile of the achieved structures and found out that the sidewalls are practically vertical (Figure 4). This suggests that calixarene patterning is different than that for the electrostatic patterning of polymers where the polymer mass transport creates a glassy, sloped sidewall.

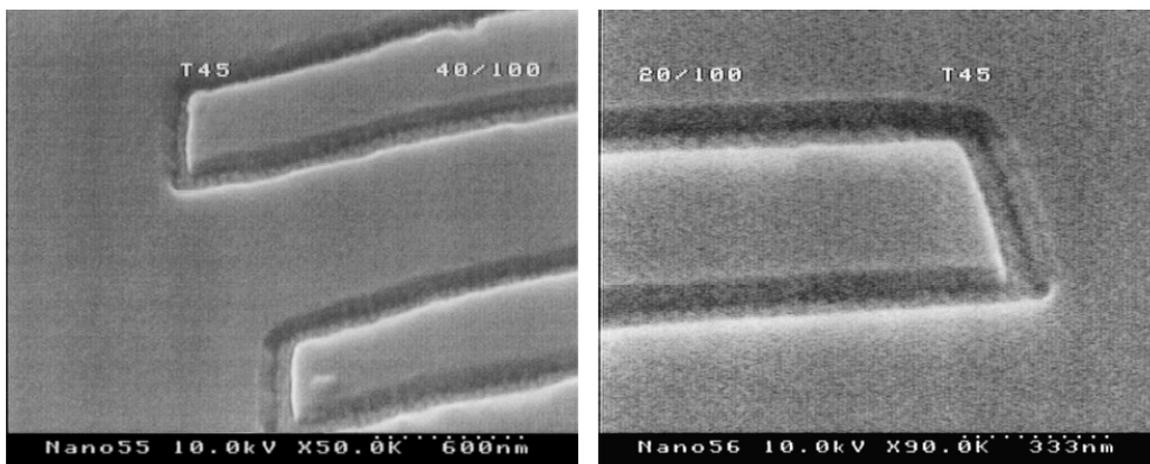


Figure 4. SEM images showing detail of the sidewalls of 30nm-line produced with electrostatic SPL using tip voltage (U_{tip}) 50V, tip current (I_{tip}) 20pA, and scanning speed 100nm/s.

We were able to generate a wide range of nanolines and nanodots in a calix[4]arene film on a Si(100) substrate, using a negatively biased AFM tip with a typical radius of 10–20 nm. The electron dose injected from a probe tip was precisely controlled using a current feedback circuit. The kinetics, growth, and optimization of the conditions for nanopatterning using electrostatic nanolithography of the polymer film

were investigated with respect to the applied potential and translational speed of the AFM tip. The experiments show that the resolution of SPM-based electrostatic lithography is influenced by the radius of the AFM tip and depends on the magnitude of tip current, the resist material, and dielectric characteristics of the polymer. Figure 5 shows typical results obtained with tip radius of approximately 10nm and 50pA; 50V and speed 200nm/s (upper two micrographs) and 100pA; 50V and speed 500nm/s (lower two micrographs).

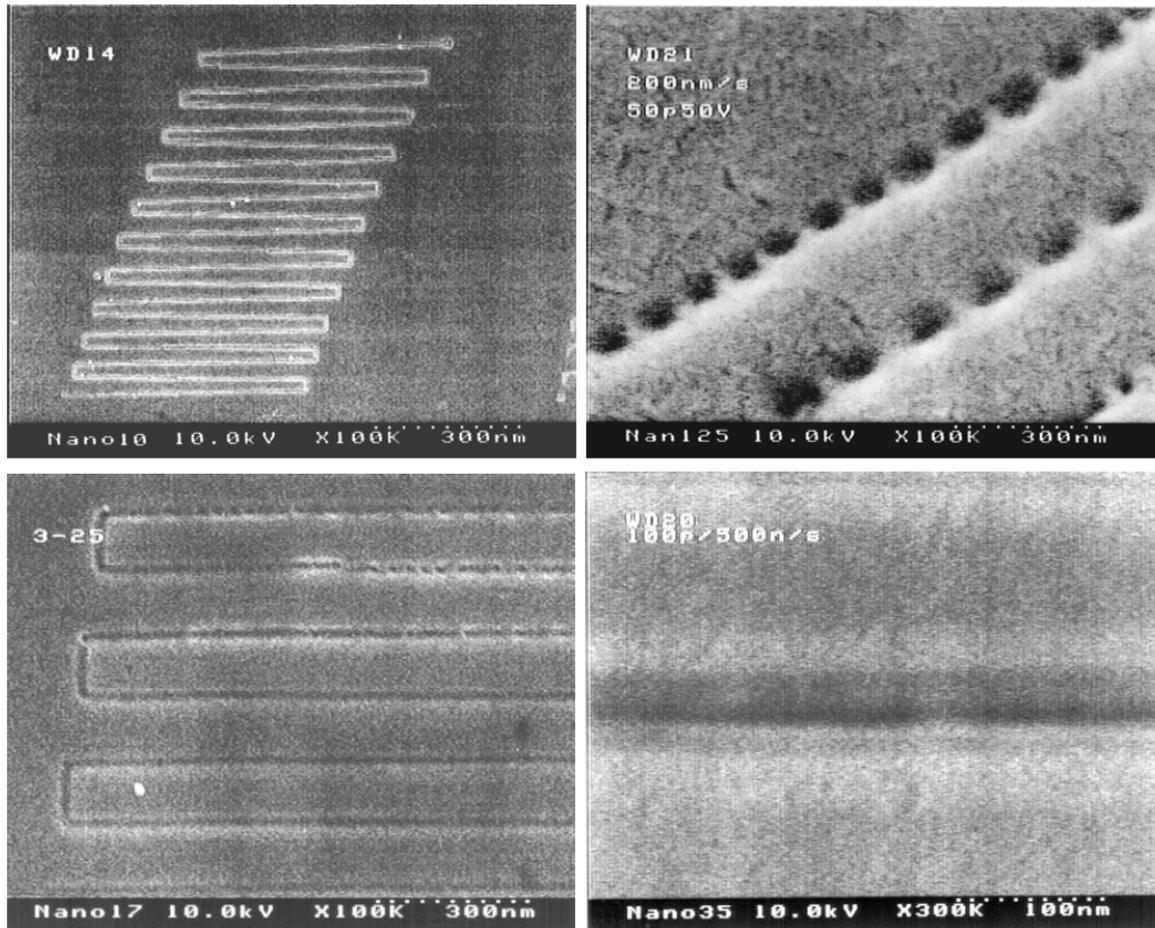


Figure 5. SEM micrographs showing 10nm-lines and dots obtained and 50pA; 50V and speed 200nm/s (upper two micrographs) and 100pA; 50V and speed 500nm/s (lower two micrographs).

We also investigated the optimal writing dose. We approach the tip to the surface and kept the current constant, holding the tip over the same point (Figure 6). Holes with a diameter of less than 10nm were

obtained at the shorter doses. At larger doses the hole diameter increases and after some time a donut is formed. We assume the donut features are formed by reverse mass transport of calixarene molecules previously attached to the tip, back to the substrate surface.

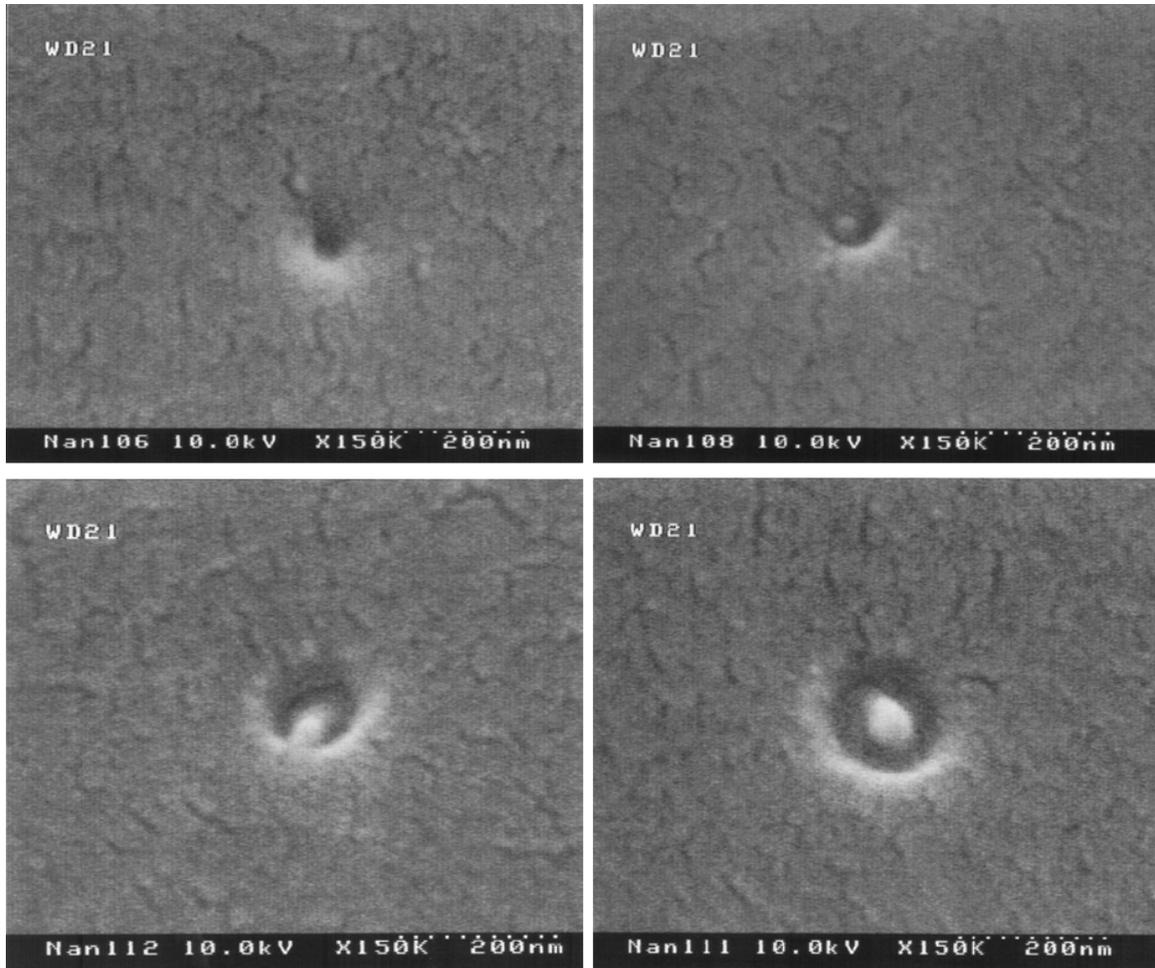


Figure 6. Delineation of single dots for different current exposure times (from left to right the time was 8, 24, 48 and 100msec and $U_{tip}=50V$, tip current $I_{tip}=20pA$). The experiment shows that at larger doses, donut structures are obtained, potentially due to reverse mass transport of calixarene molecules from the tip to the gold surface.

SUMMARY

We report the use of atomic force microscope self-actuated piezoresistive cantilevers equipped with sharp conductive tips to achieve nanoscale patterning a resist via local electrostatic extraction of molecules from calixarene resist films. This single step, direct extraction of material is an alternative to radiation based lithographies (for example, EBL and EUVL) which expose the material and form the pattern after a development step. Not only is there advantages of reduced processing steps, but issues with resist collapse during liquid development are avoided.

SPL resolution can be tuned by tip bias, current density, and scanning speed. It's capabilities include high resolution patterning, low energy operation which prevents substrate damage and proximity interactions, high resolution alignment and direct inspection. Employing parallel, self-actuated cantilever arrays can significantly increases the "writing" speed and provides a novel technology capable of high throughput patterning of future nanoelectronic devices.

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